Chapter 7

Metal-silicate partitioning systematics of siderophile elements at reducing conditions, part 2: Implications for differentiation and core compositions of Mercury and the aubrite parent body

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ABSTRACT

Differentiation of Mercury and the aubrite parent body (AuPB) is thought to have occurred at extremely reducing conditions, as implied from the low FeO and high S contents inferred for their mantles. Here, the relative mantle abundances of these elements as derived from remote sensing of the surface of Mercury and analysis of aubrite meteorites are used in conjunction with experimentally determined metal-silicate partition coefficients at reducing conditions presented in a companion paper (Chapter 6) to study the geochemical processes and outcomes of core formation in highly reduced planetary bodies. Plausible core compositions of Mercury and the AuPB are assessed, and the distribution of Si and other (non)-volatile elements during core formation are quantified. Combining the new results with previous remote sensing observations of the surface of Mercury and considering three potential bulk compositional models, it is found that its core is likely to be Si rich (>4.5 21 wt.% Si). The estimated core Si contents depend mostly on the assumption of graphite saturation in Mercury’s mantle and the type of bulk composition considered. In case of the AuPB, similar calculations for C-free conditions also yield significant quantities (>5.9–20.1 wt.%) of Si in the core, the exact amount depending of bulk composition and the fO2 during AuPB differentiation. The amount of Si in the AuPB core is, however, greatly decreased if graphite-saturation is assumed. The much lower AuPB core Si contents at graphite-saturated conditions relative to the core Si concentrations calculated for Mercury, is mainly due to an overall increase in the lithophile behavior of Si at the low P-T conditions inferred for AuPB differentiation.
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The new experimental data and related thermodynamic parameterization for predicting the C concentrations at graphite saturation of Fe-Si alloys (CCGS$_{metal}$) shows that Mercury’s mantle was likely C-saturated following formation of a Si-rich core, allowing for the separation of a graphitic flotation crust, as proposed previously from MESSENGER remote sensing observations (Peplowski et al., 2015a). The formation of a graphitic flotation crust following planetary differentiation is expected to be a natural consequence of highly reduced differentiation of larger-sized bodies with high core/mantle ratios. Due to the lower Si contents calculated for the AuPB core under graphite-saturated conditions, the formation of a graphitic flotation crust is not likely to occur in smaller-sized reduced bodies such as the AuPB and other reduced asteroids due to the higher required CCGS$_{metal}$ values. The Si-rich nature of the AuPB core for C-undersaturated scenarios is expected to have resulted in preferential partitioning of the majority of the volatile siderophile elements (VSE) into the AuPB core. However, depletions for the most volatile VSE cannot be reconciled with core formation depletion only. Their depletions in aubrites require additional depletion from (I) segregating sulfides during AuPB differentiation and/or (II) compatible behavior during mineral-melt fractionation and/or (III) loss of these elements in a vapor phase during/after AuPB differentiation.

7.1 INTRODUCTION

Mercury and the aubrite parent body (AuPB) accreted at the most reducing conditions found so far in our solar system, as implied from the inferred low FeO contents and high S abundances in their mantles and their high metal-to-silicate ratios (e.g. Casanova et al., 1993; Keil, 2010; van Acken et al., 2012; Hauck II et al., 2013; Zolotov et al., 2013; Chabot et al., 2014; Malavergne et al., 2014; Knibbe and van Westrenen, 2015; Namur et al., 2016a). At these reducing conditions, significant amounts of Si are expected to partition into their cores. In a companion paper (Chapter 6) we showed the strong effects of Si on (trace) element activities in molten metal leading to significant dependencies of their metal-silicate partition coefficients on core Si content. Chapter 6 shows that siderophile elements generally behave less siderophile with increasing Si for a given $f^{0}_{O_2}$, and that the solubility of C in Fe-rich alloys is greatly decreased with increasing Si contents.

Measurements of Mercury’s surface composition and siderophile element concentrations in aubrites, in conjunction with experimentally determined metal-silicate partition coefficients and solubility limits, could therefore provide insights into the formation and differentiation of reduced bodies. Here, the geochemical processes during and consequences of core formation were studied by parameterizing the extensive metal-silicate partition coefficient database obtained at
moderately to highly reducing conditions (Chapter 6) in conjunction with remote sensing constraints on Mercury's surface composition and compiled analyses of trace elements in aubrites.

The new data are applied to provide quantitative constraints on plausible compositions of Mercury’s core, by modelling the metal-silicate partitioning behavior of Si as a function of $fO_2$ for three end-member bulk compositions considered. Using these results, the extent to which nominally lithophile element Ti may partition into Mercury’s core is assessed, and the implications for relating measured surface compositions of Mercury to bulk Mercury compositions are discussed. Using the results from these models the geochemical feasibility of a graphitic flotation crust in Mercury’s early history (Vander Kaaden and McCubbin, 2015) is assessed. A similar approach is applied to explore plausible AuPB core masses and compositions. Using constraints on the Si contents of the AuPB core, it is assessed whether the AuPB may also have experienced graphite saturation during and/or following core formation. The latter constraints are used in conjunction with the data from Chapter 6 to derive constraints on the mechanisms of VSE depletions in the AuPB mantle during and after core-mantle differentiation of the AuPB.

### 7.2 METHODS

#### 7.2.1 Bulk compositional models for Mercury and the AuPB

Mercury's surface composition (e.g. enrichment of S and relatively low FeO) and its large core mass (~6.4% by mass) are consistent with accretion or predominantly highly reduced material (e.g. Hauck II et al., 2013; Zolotov et al., 2013). Both the Bencubbinite (CB) chondrite and high enstatite chondrite (EH) meteorite groups have been proposed as possible building blocks of Mercury, given their high Fe content (up to 70 vol.% metal) and highly reduced nature (e.g. Malavergne et al., 2010; Brown and Elkins-Tanton, 2009; Namur et al., 2016a,b).

In this study, three bulk compositions were considered (Table 7.1), based on a CB$_a$ chondritic bulk composition (Gujba; Rubin et al., 2003), a CB$_b$ chondritic bulk composition (MAC 02675; Lauretta et al., 2007) or an average EH chondritic bulk composition (Newsom, 1995). CB chondrites are divided into the CB$_a$ and CB$_b$ groups based on several aspects including textural characteristics, the amount of metal and the occurrence and volume of refractory inclusions (Lauretta et al., 2009). The CB$_a$ group is characterized by metal abundances between 40–60 vol.%., whereas specimens from the CB$_b$ group may contain over 70 vol.% metal (Rubin et al., 2003; Lauretta et al., 2007). Table 7.1 shows the inferred bulk compositions for CB$_a$ chondrite Gujba (Rubin et al., 2003) and for CB$_b$ chondrite MAC02675 (Lauretta et al., 2007). These
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compositions cover a wide range of bulk Si contents (7–17.7 wt.%) which is useful for assessment of the overall uncertainties and constraints on Mercury’s core composition. Although it is acknowledged no known meteorite group is likely fully compatible with Mercury’s inferred bulk composition, including CB chondrites (e.g. Chabot et al., 2014), very high metal abundances in Mercury’s building blocks are required to explain its large core. It is therefore reasonable to assume that Mercury’s bulk composition is not dramatically different from the composition of typical CB chondrites, unless Mercury’s mantle was removed either by one giant impact (see Benz et al., 2007) or by several smaller impacts in so-called “hit and run” collisions (Asphaug and Reufer, 2014). Although the EH chondrites contain insufficient metal to produce a Mercury-sized core, this compositional endmember is used to explore the effects of such partial removal of Mercury’s mantle by (an) impact(s) on plausible core Si concentrations.

The similarity between geochemical features of aubrites and those inferred for Mercury’s surface and interior (i.e. low FeO contents and high S contents of silicates and high overall metal contents) suggests a similar reduced bulk composition for the AuPB. Indeed, a close genetic relationship between low- and high enstatite (EL, EH) chondrites and aubrites is suggested based on their identical oxygen isotopic compositions (Clayton and Mayeda, 1996; Keil, 2010; Greenwood et al., 2018). Some workers proposed a genetic link between EL and/or EH chondrites and aubrites from other petrological and geochemical lines of evidence, such as bulk chemistry, oxygen fugacities and siderophile element abundances (Watters and Prinz, 1979; Biswas et al., 1980; Wolf et al., 1983). However, a direct genetic link between aubrites and an EH and/or EL chondritic parent body remains highly debated (Keil, 2010 and references therein). Arguments that argue against a direct genetic link between aubrites and EL and/or EH chondrites are related to (1) the low Fe,Ni metal to troilite ratios (~0.45) of aubrites, relative to high ratios (~2.6) observed in EH and/or EL chondrites and the significant differences between Ti contents of troilite in both meteorite suites; (2) the fact that most aubrites are fragmental breccias but lack EL and/or EL chondritic clasts, and vice versa (3) the differences in cosmic ray exposure ages between both groups, (4) the REE systematics of oldhamite in both groups and (5) differences between bulk compositions of metal grains in aubrites and enstatite chondrites (Keil, 2010 and references therein).

One of the aims of this study is to assess whether formation of a Si-bearing, Fe-rich core in the AuPB can result in significant depletions of the VSE. Another major aim is to determine plausible ranges of the Si contents of the AuPB core. It is later shown that these aims are not strongly dependent on the assumed AuPB bulk composition and the choice of an EH or EL-like bulk composition for the AuPB is therefore deemed sufficient for the purpose of this study.
Table 7.1 Bulk major element compositions (in wt%) assumed for Mercury (EH-CB2-CB3) and the AuPB (EH-EL)

<table>
<thead>
<tr>
<th>Bulk</th>
<th>Mg</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>S</th>
<th>Ni</th>
<th>Mn</th>
<th>Cr</th>
<th>Ti</th>
<th>O</th>
<th>nbaO*</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guiba (CB3)</td>
<td>5.6</td>
<td>7.0</td>
<td>0.63</td>
<td>0.71</td>
<td>67.3</td>
<td>0.5</td>
<td>4.75</td>
<td>0.06</td>
<td>0.30</td>
<td>0.78±0.43</td>
<td>-</td>
<td>12.4</td>
<td>2.4</td>
</tr>
<tr>
<td>MAC02675 (CB3)</td>
<td>2.2</td>
<td>11.9*</td>
<td>0.25</td>
<td>0.32</td>
<td>65.4</td>
<td>0.2</td>
<td>2.63</td>
<td>0.02</td>
<td>0.25</td>
<td>0.78±0.43</td>
<td>0.018</td>
<td>16.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Average EL</td>
<td>14.1</td>
<td>18.6</td>
<td>1.05</td>
<td>1.01</td>
<td>22.0</td>
<td>3.3</td>
<td>1.30</td>
<td>0.22</td>
<td>0.31</td>
<td>0.36</td>
<td>0.058</td>
<td>31</td>
<td>1.2</td>
</tr>
<tr>
<td>Average EH</td>
<td>10.6</td>
<td>16.7</td>
<td>0.81</td>
<td>0.85</td>
<td>29.0</td>
<td>5.8</td>
<td>1.75</td>
<td>0.16</td>
<td>0.32</td>
<td>0.40</td>
<td>0.045</td>
<td>28</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* Sr contents were not reported in this study and were thus calculated from 100% assuming measured Na to be existing as Na2O. Mg as MgO, Al as Al2O3, K as K2O, Ca as CaO, Ti as Ti2O3, Cr as Cr2O3, Mn as MnO, and Ni, Fe and S as elemental species. Note that the amount of Si found in Fe in CB chondrites is very low which justifies our approach (Lauretta et al., 2009; Rubi et al., 2003).*1 Independent estimate from Grady and Wright (2003).*2 Calculated using Eq. (4.3), for reported bulk Mercury mantle compositions based on the corresponding chondritic components (Brown and ElkinsTanton, 2009; Namur et al., 2018b). References: [1] Rubin et al. (2003); [2] Gady and Wright (2003); [3] Brown and Elkins-Tanton (2009), while assuming a CB chondritic mantle bulk composition.[4] Lauretta et al. (2007)[5] Newsom (1995)

7.2.2 Estimation of VSE depletions in auabrites

To derive constraints on the abundances of VSE in auabrites, compiled Radiochemical Neutron Activation Analysis (RNAA) analyses were used for auabrites Aubreite, Bishopville, Bustee, Khor Timiki, Maya Belwa, Norton County, Peña Blanca Spring (Biswa et al., 1980; Wolf et al., 1983). These auabrites have been classified as fragmental breccias or regolith breccias and show no evidence for having an origin from a parent body other than the AuPB (Keil, 2010; Table A.7.1). The results for the Shallowater auabrite were excluded, given the fact that it was likely derived from a different parent body than all other auabrites (Keil et al., 1989; Keil, 2010).

Due to the extremely heterogeneous nature of auabrites in terms of troilite, oldhamite and/or Fe,Ni distribution (Keil, 2010; van Acken et al., 2012a), measured Ag and/or Ir concentrations were used to monitor metal contamination within each of the analyses (van Acken et al., 2012b).

Measurements that contained >1 ppb Ir were excluded. Given the abundance of 1 to 4 ppm Ir measured in metal nodules in several different auabrites (Casanova et al., 1993), this constrains the maximum metal contribution to less than 0.001 mass % (Table A.7.1). The measurements with <1 ppb yield an average of 30 ppb Ag, with an upper limit of 85 ppb. Although Biswas et al. (1980) did not determine Ir contents in their RNAA analyses, the fact that all of their reported Ag concentrations in auabrites are lower than ~60 ppb suggest that their VSE measurements were not hampered by incorporation of meaningful quantities of Fe,Ni metal.

Van Acken et al. (2012b) reported analyses of sulfides and metals in auabrites and showed that auabritic sulfides are HSE-poor. To assess the extent of sulfide incorporations within the analyses of Biswas et al. (1980) and Wolf et al. (1983), Te abundances were used. Sulfide-silicate partitioning experiments (e.g. Rose-Weston et al., 2009; Steenstra et al., 2018b) show that Te is highly chalcophile at reducing conditions. This is confirmed by troilite analyses in Shallowater reported by van Acken et al. (2012b) that yielded ~7.7 to 10 ppm Te. Analyses with Te concentrations >100 ppb were removed, which in turn corresponds with a maximum of 0.01 mass % of sulfide incorporation within those measurements. Given the concentrations for Te reported by Biswas et al. (1980) and Wolf et al. (1983), it is unlikely that sufficient sulfides were
incorporated in these measurement to distort the concentrations of mostly more abundant and far less chalcophile elements (Co, Ni, Ga, Ge, In, As, Sb; van Acken et al., 2012b; Wood et al., 2014; Steenstra et al., 2018b).

### 7.2.3 Prediction of D during core formation in Mercury and the AuPB

To obtain a predictive model for Si partitioning during core formation in Mercury and the AuPB, the apparent exchange coefficient of Si or log $K_{app}$, was considered:

$$\log K_{app} = \log \left( \frac{x_{\text{silicate}}}{(y_{\text{SiO}_2})} \cdot \frac{(y_{\text{metal}})}{(x_{\text{FeO}})} \cdot \frac{(x_{\text{Fe}})}{(y_{\text{FeO}})} \cdot \frac{(x_{\text{SiO}_2})}{(y_{\text{silicate}})} \right)$$

(7.1)

where $x$ is the molar fraction and $y$ are the activity coefficients of Fe(O) and Si(O$_2$) in the metal and silicate melts, respectively. For additional details on the thermodynamic background of Eq. 7.1, the reader is referred to Chapter 6. The log $K_{app}$ Si values from the dataset of Chapter 6 are combined with literature data (Kilburn and Wood, 1993; Wade and Wood, 2001; 2005; Malavergne et al., 2007; Corgne et al., 2008; Mann et al., 2009; Ricolleau et al., 2011; Shahar et al., 2011; Tuff et al., 2011; Bouhifd et al., 2007, 2013; Cartier et al., 2014; Hin et al., 2014; Fischer et al., 2015; Wang et al., 2016; Righter et al., 2017b) and parameterized to:

$$\log K_{app} = a + b(1/T) + c(P/T) + d_1(\text{nbo}/t)$$

(7.2)

where $a$, $b$, $c$, $d_1$ are regression constants, $T$ is temperature in K, $P$ is pressure in GPa and parameter $\text{nbo}/t$ represents the molar ratio of non-bridging oxygen per tetrahedrally coordinated cations in the silicate melt (Eq. 4.3). The $\text{nbo}/t$ parameter is over-simplifies the complex effects of silicate melt composition on metal-silicate partitioning of most siderophile elements (O’Neill and Eggins, 2002; Steenstra et al., 2017b). Although the use of a regular solution model (RSM) is preferred to constrain the effect of individual silicate melt compositional parameters (e.g. Tuff et al., 2011), the number of variables required for this approach would greatly over-fit the metal-silicate partitioning data given the overall uncertainties in the bulk composition of Mercury and the AuPB. To test the sensitivity of the models to uncertainties in the effects of silicate melt composition, the data was also regressed without silicate melt compositional terms using a highly simplified version of a regular solution model (Burkemper, 2013):

$$\log K_{app} = a + b(1/T) + c(P/T) + d_2(x_{\text{SiO}_2})^2 + d_3(x_{\text{CaO+MgO}}) + d_4(x_{\text{CaO+Al}_2O_3})$$

(7.3)

The data was also parameterized using subsets obtained for three different pressure regimes (>5 GPa only, covering the pressure regime of Mercury’s mantle; ~5 GPa, and all pressures).
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Due to an overall lack of activity parameters which prevents the use of $K_{\text{app}}$-based parameterizations, regressions for Ti were performed for $\log D_{\text{Ti}}^{*}$ values obtained at <5 GPa using a multilinear-regression parameterization that includes metal compositional parameters for C and Si, while assuming a 4+ valence state:

$$\log D_{\text{Ti}}^{*} = a + a_2(\Delta IW) + b(1/T) + c(P/T) + d_1(nbo/t) + e(1 - x_{\text{metal}}^{\text{metal}}) + f(1 - x_{\text{Si}}^{\text{metal}}) \quad (7.4)$$

where parameters $x_{i}^{\text{metal}}$ represent the molar fractions of component $i$ in the metallic alloy and mimic the Margules interaction parameters. For comparison purposes, $D_{\text{Ti}}^{*}$ was also regressed without silicate melt compositional terms and using a simplified version of the RSM (Table 7.2).

In all regressions $\gamma_{\text{FeO}}^{\text{silicate}}$ was assumed to be unity, given that no predictive model is available for describing variations in $\gamma_{\text{FeO}}^{\text{silicate}}$ at very low $fO_2$. For the most reduced experiments discussed in Chapter 6, the calculated $\gamma_{\text{FeO}}^{\text{silicate}}$ values based on the offset between $\Delta IW$ and $\Delta Si-SiO_2$ (see Table 6.1 in Chapter 6) were used. The large majority of data from other previous studies has distinctly higher $\Delta Si-SiO_2$ values and do not show such offsets. The $\gamma_{\text{FeO}}^{\text{silicate}}$ values are therefore unlikely to be significantly different from unity.

The $\log K_{\text{app}} Si^{4+}$ values were calculated assuming the interaction parameters listed in the online metal activity calculator (Tuff et al., 2011), as these values are within error of those reported in Chapter 6. Note that the small pressure effects on the interaction coefficient of Si in Fe-Si alloys reported in Chapter 6 do not significantly affect our results. Table 7.2 lists the results of the regressions. It was found that for Si the addition of (a) silicate melt compositional term(s) greatly improve(s) the overall fit, consistent with previous studies that reported strong silicate melt compositional effects on the partitioning of Si (Tuff et al., 2011; Ricolleau et al., 2011). The temperature dependence term of $-17409(1420)$ is in good agreement with the proposed 1/T term of $-14338$ for $\log K_{\text{app}} Si^{4+}$ assuming 1 atm thermodynamic data (Tuff et al., 2011). Given the similar outcome of the parameterizations of $K_{\text{app}} Si^{4+}$ with $nbo/t$ and the simplified RSM, the $nbo/t$ parameterization is used in models of the interior compositions of Mercury and the AuPB. The choice to only include <5 GPa data becomes evident from the results of the regressions, that show that the pressure dependency of $K_{\text{app}} Si$ below 5 GPa is distinctly different than that for >5 GPa data) (Table 7.2, Fig. A.1). A difference in the pressure dependency is most likely due to a major structural transition in Fe-rich liquids at approximately 5 GPa (Sanloup et al., 2011). Because the pressure for both Mercury and the AuPB core-mantle boundary is estimated to be 5 GPa or lower, the <5 GPa parameterization is used for Si.
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For Ti, P-T effects are small relative to the effects of Si and C in the metal (Table 7.2). Silicate melt composition, approximated by nbo/t, was found to be statistically insignificant. Fig. A.2 provides a comparison between measured and predicted D values. The parameterizations are of acceptable quality for the purpose of this study, given the limited number of fit parameters and the overall uncertainties in the bulk composition of Mercury and the AuPB.

To obtain D*M, Equation (7.2) can be converted to:

\[
\log D'_M = a + b(1/T) + c(P/T) + d_1(nbo/t) - n/2 \log(x_{FeO}^{Silicate}/x_{Fe}^{Metal}) - \log (\gamma_M^{metal}/(\gamma_{Fe}^{metal})^{\delta_2})
\]  

(7.5)

where fO2 is now represented by the last two terms.

To predict the variability of the metal-silicate partitioning of the VSE as a function of Si contents of the metal, the newly derived 1 GPa - 1883 K interaction coefficients were used as reported in Chapter 6. As discussed in the next section, these P-T conditions are close to or directly relevant for modeling core formation in the AuPB. For Se and Te, no interaction coefficients can be derived due to their unique dependency on fO2 (Rose-Weston et al., 2009; Chapter 6). Their metal-silicate partitioning behavior at 1 GPa and 1883 K was constrained as a function of fO2 using polynomial fits, yielding R² values of >0.98. The models for Se and Te are graphically illustrated in Fig. 6.8. Correction of the 1 GPa fits from Chapter 6 to the modeled 0.1 GPa value used for the AuPB using the pressure dependencies on log D_{Se,Te}^{metal-sil} from Steenstra et al. (2017c), yields the following equations: \[ \log D_{Se}^{metal-sil} = -0.1232 \ast (\Delta IW)^2 - 0.5149 \ast \Delta IW + 0.21 \pm 0.06; \ R^2 = 0.99; \ \log D_{Te}^{metal-sil} = -0.1565 \ast (\Delta IW)^2 - 0.8260 \ast \Delta IW + 0.05 \pm 0.05; \ R^2 = 0.98. \]

### 7.2.4 Modeling core formation in Mercury and the AuPB

Using the newly derived expressions and/or interaction coefficients, the D or K0 values were calculated for a given fO2 in the range –8 < ΔIW < –3 using Eqs. (7.2, 7.5) for Si, Eq. (7.4) for Ti and Eqs. 4.2, 6.1–6.3 for the VSE (Table 7.2). In all modeling scenarios, parameters \( \gamma_{Fe}^{metal} \) and \( \gamma_{Si}^{metal} \) were calculated for the expected Si core concentrations using the online metal-activity calculator (Wade and Wood, 2005). Activities were calculated assuming C-free or C-saturated conditions, depending of the modeled scenario. This approach yields corrected core compositions that take all interactions between the different elements into account. The fO2 values were also corrected for different \( \gamma_{Fe}^{metal} \) and Fe abundances in each scenario. The D values were then recalculated considering the calculated changes in activity coefficients. Note that it has been shown that the interaction parameter of Si in Fe-Si alloys is only slightly dependent on pressure within the 2–4 GPa range and is within error of values reported in the
online metal activity calculator. The online metal activity calculator (Wade and Wood, 2005) was therefore used to calculate the activities of Si for the different bulk compositions, required to calculate its metal-silicate partition coefficients for a given $f_{O_2}$ value. Interaction parameters for VSE in Fe-Si alloys were calculated using the 1 GPa - 1883 K interaction coefficients for each of the modeled elements reported in Chapter 6. The $K_0$ values were then modeled as a function of metal composition using the approach outlined in Chapter 6.

For Mercury and the AuPB, the C contents of Fe-Si metals at graphite saturation were calculated using the expression for CCGS$_{metal}$ (Eq. 6.6) as reported in Chapter 6. To calculate the metal-silicate partition coefficient of C as a function of $f_{O_2}$ and Si content of the alloy, the model of Li et al. (2016) was used that is appropriate for conditions more reducing than $\Delta IW = -1.5$. The D values and CCGS$_{metal}$ values applicable to core formation in Mercury were calculated assuming a core-mantle boundary pressure of 5 GPa and a liquidus temperature for Mercury’s magma ocean of 2200 K at 5 GPa (Namur et al., 2016b). For modeling of core formation in the AuPB, a metal-silicate equilibration temperature of 1883 K and a pressure of 0.1 GPa were considered, corresponding to a core/mantle boundary pressure of a Vesta-sized body (Wilson and Keil, 1991). The VSE partitioning data used in our calculations was obtained at 1 GPa. The absence or limited offset of 1 to 2.5 GPa VSE partitioning data presented in Chapter 6 suggests that pressure effects on VSE partitioning are (near)-negligible within the 0.1 to 1 GPa range. Exceptions are elements Se and Te, for which metal-silicate partition coefficients strongly vary as a function of pressure. As discussed above, their 1 GPa metal-silicate partition coefficients were extrapolated to the modeled pressure using the pressure terms described in Steenstra et al. (2017c).

The nbo/t values were assumed to be 1.2 for the EH - EL chondritic bulk compositions and 2.4 for both CB chondritic bulk compositions (Table 7.1; Brown and Elkins-Tanton, 2009; Namur et al., 2016b). Given the lack of a predictive model for $\gamma^{silicate}_{FeO}$ for a Mercury or AuPB-like composition at highly reducing conditions, $\gamma^{silicate}_{FeO}$ was assumed to be constant ($\gamma^{silicate}_{FeO} = 1$) across the entire modeled $f_{O_2}$ range. In the calculations a Mercury core fraction of 0.67 is assumed, based on its present-day moment of inertia (Hauck II et al., 2013). For the AuPB, the specific core fractions calculated for an EH or EL chondritic bulk composition (0.395±0.015 and 0.275±0.015, respectively). Calculations summarized in Appendix Figure A.7.3 indicate that at the reducing conditions inferred for core formation in Mercury and the AuPB, the core mass is essentially independent of $f_{O_2}$, i.e. all Fe is partitioned into the core. The core fraction only varies slightly as a function of its composition.
Table 7.2 Multiple linear regression coefficients obtained using Eqs. (7.2, 7.3) for Si and Eq. (7.4) for Ti on compiled dataset and newly reported experimental metal-silicate partition coefficients. Parameterizations in bold were used for modeling.

<table>
<thead>
<tr>
<th>log ( K_{npv} )</th>
<th>a(1/T)</th>
<th>b(1/T)</th>
<th>c(PPT)</th>
<th>d(a)</th>
<th>d(b)</th>
<th>d(c)</th>
<th>d(d)</th>
<th>d(e)</th>
<th>d(f)</th>
<th>e</th>
<th>f</th>
<th>N</th>
<th>( R^2 )</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;5 GPa)</td>
<td>-3.24(75)</td>
<td>-9702(1402)</td>
<td>375(138)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>136</td>
<td>0.31</td>
<td>-</td>
<td>-13</td>
<td></td>
</tr>
<tr>
<td>(&lt;5 GPa)</td>
<td>-2.30(123)</td>
<td>-17409(1423)</td>
<td>500(108)</td>
<td>-0.707</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>136</td>
<td>0.59</td>
<td>-</td>
<td>-13</td>
<td></td>
</tr>
<tr>
<td>(&lt;5 GPa)</td>
<td>-2.90(98)</td>
<td>-1393(1689)</td>
<td>450(86)</td>
<td>6.28(45)</td>
<td>n.s.s. (^b)</td>
<td>n.s.s.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>136</td>
<td>0.72</td>
<td>-</td>
<td>-13</td>
</tr>
<tr>
<td>(&gt;5 GPa)</td>
<td>-3.11(91)</td>
<td>-9888(1980)</td>
<td>157(29)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67</td>
<td>0.68</td>
<td>-</td>
<td>-3,5,6,9,11-17</td>
<td></td>
</tr>
<tr>
<td>(&gt;5 GPa)</td>
<td>1.92(35)</td>
<td>-14289(2473)</td>
<td>74(37)</td>
<td>-0.341(11)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67</td>
<td>0.73</td>
<td>-</td>
<td>-3,5,6,9,11-17</td>
<td></td>
</tr>
<tr>
<td>(&gt;5 GPa)</td>
<td>0.43(139)</td>
<td>-1768(1923)</td>
<td>92(31)</td>
<td>5.77(14)</td>
<td>n.s.s. (^b)</td>
<td>n.s.s.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67</td>
<td>0.75</td>
<td>-</td>
<td>-3,5,6,9,11-17</td>
</tr>
<tr>
<td>(all)</td>
<td>-3.10(96)</td>
<td>-5546(1088)</td>
<td>199(24)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>203</td>
<td>0.65</td>
<td>-</td>
<td>-17</td>
<td></td>
</tr>
<tr>
<td>(all)</td>
<td>1.90(74)</td>
<td>-1641(1291)</td>
<td>56(22)</td>
<td>-0.536</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>203</td>
<td>0.75</td>
<td>-</td>
<td>-17</td>
<td></td>
</tr>
<tr>
<td>(all)</td>
<td>-2.23(16)</td>
<td>-12306(1067)</td>
<td>91(18)</td>
<td>-5.50(48)</td>
<td>n.s.s.</td>
<td>-22.92(933)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>203</td>
<td>0.82</td>
<td>-</td>
<td>-17</td>
</tr>
</tbody>
</table>


Table 7.3 Modeled interior compositions for Mercury. Compositions were modeled assuming a core mass of 67%, a pressure of 5 GPa and a temperature of 2200 K during core-mantle differentiation and assuming either C-free or C-saturated conditions. Reported compositions are based on the \(\Delta V\) range of −5.4±0.4 assuming non-ideal activities of Fe in the metal and ideal activities of FeO in the silicate melt.

<table>
<thead>
<tr>
<th>Calculated compositions</th>
<th>Core Fe (wt.%)</th>
<th>Ni</th>
<th>C*</th>
<th>Si</th>
<th>CCBS(_{metal})</th>
<th>Mantle Si (%)</th>
<th>Fe</th>
<th>Ti</th>
<th>C (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EH (c-free)</td>
<td>76.6±1.2</td>
<td>2.61</td>
<td>-</td>
<td>19.2±1.2</td>
<td>10.3±0.17</td>
<td>0.11±0.07</td>
<td>0.136±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EH (c-saturated)</td>
<td>78.0±2.0</td>
<td>0.69</td>
<td>0.59</td>
<td>18.7±1.8</td>
<td>0.46±0.19</td>
<td>13.2±3.7</td>
<td>0.09±0.03</td>
<td>0.136±0.01</td>
<td>57±21</td>
</tr>
<tr>
<td>CB(_b) (c-free)</td>
<td>83.5±0.5</td>
<td>7.08</td>
<td>-</td>
<td>9.4±0.5</td>
<td>2.1±1.1</td>
<td>0.24±0.12</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CB(_b) (c-saturated)</td>
<td>85.2±2.6</td>
<td>7.08</td>
<td>1.15±0.05</td>
<td>6.5±1.8</td>
<td>3.1±0.11</td>
<td>0.14±0.03</td>
<td>-</td>
<td>-</td>
<td>29±20</td>
</tr>
<tr>
<td>CB(_f) (c-free)</td>
<td>80.5±0.9</td>
<td>3.92</td>
<td>-</td>
<td>15.3±0.9</td>
<td>3.8±1.1</td>
<td>0.22±0.12</td>
<td>0.04±0.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB(_f) (c-saturated)</td>
<td>83.8±3.3</td>
<td>3.92</td>
<td>1.15±0.05</td>
<td>11.1±2.6</td>
<td>2.8±0.009</td>
<td>0.12±0.03</td>
<td>0.036±0.004</td>
<td>46±40</td>
<td></td>
</tr>
</tbody>
</table>

Mantle ratios \(^c\) Fe/Si\(_{SI}\) calc. Mg/Si\(_{SI}\) calc. Ti/Al\(_{SI}\) calc. Al/Si\(_{SI}\) calc. Ca/Si\(_{SI}\) calc.

| EH (c-free)             | 0.07±0.01      | 0.012±0.009 | 0.46±0.12 | 3.9±0.79 | 0.014±0.003 | 0.050±0.000 | 0.24±0.02 | 0.25±0.06 |       |
| EH (c-saturated)        | -               | 0.009±0.006 | -         | 3.0±0.90 | 0.050±0.000 | -         | 0.23±0.07 | 0.22±0.07 |       |
| CB\(_b\) (c-free)       | -               | 0.075±0.059 | -         | 11.3±5.8 | 0.27±0.11 | 0.13±0.007 | 1.43±0.74 |       |
| CB\(_b\) (c-saturated) | -               | 0.011±0.007 | -         | 2.3±0.96 | 0.020±0.000 | -         | 0.09±0.03 |       |
| CB\(_f\) (c-free)       | -               | 0.006±0.005 | -         | 0.2±0.18 | 0.020±0.000 | -         | 0.02±0.01 |       |
| CB\(_f\) (c-saturated) | -               | 0.003±0.002 | -         | 0.2±0.09 | 0.020±0.000 | -         | 0.03±0.01 |       |

\(^c\) Calculated using the predictive model of Li et al. (2016) \(^c\) Calculated using Eqs. (6.6) assuming the computed Ni and Si contents and T = 2200 K \(^c\) Fe/Si\(_{SI}\) ratios were calculated assuming the FeO contents corresponding to \(\Delta V\) = −5.4±0.4, while assuming non-ideal \(y_{metal}\) and ideal \(y_{silicate}\) or each scenario (see sections 2.3, 2.4). Major element abundances in all scenarios were calculated considering only Si, Al, Ca, Mg, Fe, Ti and S and assumed to be present as SiO\(_2\), Al\(_2\)O\(_3\), CaO, MgO, TiO\(_2\) and elemental S References: [1] Weider et al. (2014) [2] Evans et al. (2012) [3] Weider et al. (2012) [4] Peklova et al. (2012)
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Full chemical equilibrium between the core and mantle of Mercury and the AuPB is assumed, i.e. in a global magma ocean setting (Taylor et al., 1993; Brown and Elkins-Tanton, 2009). This is a reasonable assumption given the expected availability of short-lived radiogenic heat producing elements during the inferred early differentiation of the AuPB (Keil, 2010 and references therein). Although aubrites are difficult to date due to the mono-mineralic nature of these rocks (Keil, 2010), it is well established that the AuPB parent body accreted very early. For example, Shukolyukov and Lugmair (2004) studied the $^{54}$Mn-$^{53}$Cr systematics of three aubrites (Peña Blanca Spring, Bishopville and Cumberland Falls) and reported excess $^{53}$Cr in Peña Blanca Spring (i.e. $^{54}$Mn was still extant curing crystallization of this aubrite). The excess $^{53}$Cr corresponds to a model age of 4564-4552 Ma and shows that the AuPB experienced global differentiation, including core formation, very early in the history of the solar system. A global magma ocean setting on the AuPB with a liquidus temperature of 1850 K has also been suggested from consideration of igneous rock fragments in aubrites (Taylor et al., 1993) and it is required for the extensive metal segregation in the AuPB proposed by Lodders et al. (1993) and Casanova et al. (1993).

Under these assumptions, the core and mantle abundances of the various elements are calculated using the following mass balance equations:

$$C_{\text{mantle}}^i = \frac{C_{\text{bulk planet}}^i}{x_{\text{mantle}} + (1 - x_{\text{mantle}}) * D(i)}$$ \hspace{1cm} (7.6)

$$C_{\text{core}}^i = \frac{C_{\text{bulk planet}}^i}{x_{\text{core}} + (1 - x_{\text{core}})/D(i)}$$ \hspace{1cm} (7.7)

where $C_{\text{mantle}}^i$, $C_{\text{core}}^i$ and $C_{\text{bulk planet}}^i$ are the concentrations of element $i$ in the mantle, core or bulk of Mercury or the AuPB, $x_{\text{core}}$ and $x_{\text{mantle}}$ represent the respective core and mantle mass fractions for both bodies and $D(i)$ represents the metal-silicate partition coefficient for element $i$. The $D$ values required to fully explain the observed depletions of the various VSE in aubrites by core formation, or $D_{\text{in}}^i(i)$, are calculated with Eq. (3.7).

A recent study suggested that graphite is present at various locations across Mercury's surface (Peplowski et al., 2016). This suggests that Mercury's interior, and possibly those of other reduced planets, could have been graphite saturated in their early history. The $D$ values and corresponding activities for the elements considered were therefore calculated for either C-free and C-saturated conditions. Due to the lack of interaction coefficients for VSE in C-rich alloys, only C-free conditions were considered for modeling of VSE depletions in the AuPB. Light elements in the cores of Mercury and the AuPB other than Si and C were not considered, as the inferred $f/0_2$ is too low to allow for significant partitioning of $S$ or $U$ (Kilburn and Wood, 167
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1997; Ricolleau et al., 2011). The effects of Ni were considered, given its effects on CCGSMet. Due to its overall siderophile behavior, virtually all available Ni present in the bulk of Mercury and the AuPB will partition into its core within the P-T range and fO2 range considered here.

The above models vary as a function of fO2. Independent constraints on the redox state of Mercury’s interior are provided by the measured S contents of Mercury’s surface of 1.4 to 2.6 wt.% for the CBI terrain and high-Mg region, respectively (Peplowski et al., 2015a). These measurements, combined with experimentally determined S concentrations at sulfide saturation (SCSS) at low fO2 conditions, have been used to argue for conditions of ΔIW = −3.4 to −6.6 (Namur et al., 2016a). More than ~75% of the measured chemical compositions are compatible with a more reducing and narrower range of ΔIW = −5.4±0.4 (Namur et al., 2016a), which will be used in the remainder of this study. Watters and Prinz (1979) proposed bulk aubritic compositions using modal data and reported FeO contents ranging between 0.02 to 0.07 wt.% in the various aubrites considered. Although it is important to realize that aubrites are not primary melts, the low FeO contents of aubritic enstatites, diopsides and forsterites must relate to very low FeO contents of their source regions (Fogel, 1998). Indeed, Fogel (2005) later reported FeO contents ranging between 0.15 to 0.26 wt.% for aubritic basalt vitrophyres and considered these components to be the “missing” basalts from the AuPB. The range of 0.15 to 0.26 wt.% FeO was therefore considered to be representative of that of the redox state of the AuPB mantle. This FeO range corresponds to an overall fO2 range of ~ΔIW = −5.8 to −5.2, the exact value depending of the amount of Si that is partitioned into the AuPB core and its effect on yFe^2+. The latter fO2 range will be used throughout the study in the discussion of the expected AuPB core Si content and expected VSE depletions through formation of a core.

7.2.5 Remote sensing constraints on Mercury’s surface composition
Table 7.3 summarizes remote sensing constraints on Mercury’s surface composition relevant to this work. Mercury’s surface has an average Si content of ~25 wt.% (Peplowski et al., 2015b). The exact amount varies for each of the different terrains considered. The lowest Si content of ~23.8 wt.% is inferred for the high-Mg region, whereas the northern terrain is thought to be the most Si-rich terrain with ~27.5 wt.% (Peplowski et al., 2015b). Absolute abundances of Ti on Mercury’s surface are constrained to a maximum of 0.8 wt.% (Peplowski et al., 2015a), with lower values more likely if C is abundant on the surface. Surface Ti/Al ratios are 0.0048±0.0013 on average (Weider et al., 2014) and this value will be used in the models discussed in section 7.3.1.1. For comparison of the model outcomes with the observed surface ratios, major element

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ratio estimates (Fe/Si, Ca/Si and Mg/Si) based on X-ray (XRS) spectrometer and gamma ray spectrometer (GRS) measurements are also listed in Table 7.3.

7.3 RESULTS

7.3.1 Constraints on interior composition and differentiation of Mercury

7.3.1.1 Nominally lithophile element contents of Mercury’s core and/or mantle

Figure 7.1 shows core and mantle abundances of Si and C for different core formation scenarios and considering the three end-member bulk compositions for Mercury. At $\Delta IW = -5.4 \pm 0.4$, significant amounts of Si partition into the core in all considered scenarios, with values ranging from $\approx 4.5$ to as much as 21 wt.%. For all scenarios the corresponding mantle Si abundances are lower than remote sensing observations of Si on Mercury’s surface (Pepowski et al., 2015b) (Table 7.3). Assuming a C-saturated core results in higher Si contents of Mercury’s mantle, but values are still lower than the observed range of Si on Mercury’s surface (Fig. 7.1). Core-mantle differentiation scenarios that predict a lower bulk silicate Mercury content than observed on the surface are likely, because differentiation of bulk silicate Mercury after core formation would have led to an increase in surface Si content (Brown and Elkins-Tanton, 2009; Knibbe, 2018). Mantle differentiation after core-mantle differentiation of Mercury’s mantle is also required from consideration of Fe/Si, Mg/Si and Ti/Al ratios (Table 7.3). For example, observed surface Mg/Si ratios are in most cases significantly lower than ratios derived from core-mantle differentiation models. The CB$_{26}$ bulk composition yields Mg/Si values in the range of those proposed from surface remote sensing observations (Weider et al., 2012). This bulk composition also yields Fe/Si, Al/Si and Ca/Si ratios that are far below those measured on Mercury’s surface.

The EH and CB$_{26}$ bulk compositions yield Ti/Al, Al/Si, Ca/Si ratios that are within the range of remote sensing observations, but predict considerbly higher silicate Mg/Si and/or mostly much lower Fe/Si ratios than observed at the surface (Table 7.3). These systematics can be reconciled by significant magmatic differentiation during the magma ocean-stage and/or later secondary magmatism (Namur et al., 2016b). Namur et al. (2016b) proposed an overall decrease of Mg/Si from $\approx 0.75$ in the mantle to $\approx 0.20$ at the surface, by modelling mantle melting of an EH4 chondritic bulk composition. The lower silicate Fe/Si values calculated for virtually all scenarios could be related to the presence of Fe in sulfides, which are likely a late stage crystallization product and may enhance Fe on the surface relative to Mercury’s interior (McCoy et al., 1000; Zolotov et al., 2013). This would also enhance the $S$ concentration in the crust relative to Mercury’s interior. This effect would be less pronounced for $S$ than for Fe, given that
its average modeled abundance on Mercury’s surface is up to 1 order of magnitude higher (Hauck II et al., 2013).

Our models indicate that titanium may behave siderophile during core formation in Mercury, depending on the core Si content (Fig. 7.2; Table 7.3). For the CB₉ and CB₁₀ bulk compositions, the calculated D⁰ₜₐ values are around 0.2 to 3, depending on the fO₂ and the assumption of C saturation. These D values would yield a Ti mantle depletion of up to ~25% of the total mantle budget through core formation, resulting in lower mantle Ti/Al ratios relative to bulk Mercury values. In case of the EH composition Ti behaves lithophile (D⁰ₜ = 0.001–0.0025). Table 7.3 shows that all modeled bulk silicate Mercury Ti/Al values are much higher than surface Ti/Al ratios derived from remote sensing measurements. This may suggest that Ti preferentially partitioned into sulfides during solidification of Mercury’s magma ocean, as proposed by Cartier et al. (2017). The possible formation of a FeS layer in Mercury’s deep interior, which is currently debated (e.g. Hauck II et al., 2013; Knudde and van Westrenen 2018; Cartier et al., 2017), further increases the complexity of relating surface Ti abundances to a bulk Mercury composition, as the sulfide-silicate partitioning of Ti is expected to be a function of P-T and fO₂ - which in turn depend on the depth at which the FeS layer formed.

7.3.1.2 The formation of a graphite flotation crust in Mercury’s early history

The core Si contents calculated for each of the models described in section 7.3.1.1 were used to compute CCGS_metal values for Mercury’s core at 5 GPa and 2200 K using Eq. (6.6). Results are shown in Fig. 7.4. To compare these CCGS_metal values with the predicted core C abundances for the different bulk compositions, metal-silicate partition coefficients for C were calculated using the expressions of Li et al. (2016) at 5 GPa and 2200 K. These calculations were performed for each given Si content of Mercury’s core and corresponding fO₂. The solubility of C in Mercury’s core was found to be <4.4 wt.% (Fig. 7.4; Table 7.3) at conditions more reducing than ΔIW = -5. At ΔIW = -5.8, the solubility of C in Mercury’s core is significantly decreased due to increasing Si contents of Mercury’s core.

The combination of the overall limited solubility of C in Fe-Si alloys and the low solubility of C in highly reduced silicate melts (~50 ppm C at ΔIW = -5.5; Li et al., 2016), implies that Mercury’s mantle may have been graphite saturated upon differentiation (Table 7.3). Whether this occurs is, however, strongly dependent of 1) the C concentration in bulk Mercury and 2) the Si and to a lesser extent the Ni content of Mercury’s core. Although there are no quantitative constraints on the C concentration in bulk Mercury, it is evident that only limited amounts of C are required to yield graphite saturation, if Mercury’s core contains significant amounts of Si.
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This is illustrated in Fig. 7.4, which shows that at high (~19 wt.%) Si concentrations, only ~0.5 wt.% C in Mercury’s core is required to reach C saturation. At 6 wt.% Si, this is increased to ~4 wt.% C. In case of an EH bulk composition with the corresponding 19 wt.% Si core, a bulk Mercury C content of ~0.18 wt.% would be required to generate graphite saturation of Mercury’s core. This is increased to ~2 wt.% C in case of the CB_a bulk composition, whereas consideration of the CB_b bulk composition yields ~1.3 wt.% C.

![Graph showing Si abundances in Mercury's core and mantle assuming C-free and C-saturated conditions for the three bulk compositions considered at 2200 K and 5 GPa (Table 7.3). Vertical shaded bars represent the estimated average f_O2 value of ΔIW = −5.4±0.4 of Mercury's surface (Namur et al., 2016a) Horizontal shaded bars represent the estimated Si surface content of ~25 wt % based on remote sensing observations (Peplowski et al., 2015b).]
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Fig. 7.2 The calculated \( \log D_\text{met-sil} \) values (Eq. 7.4) for the three bulk compositions considered for C-free and C-saturated conditions as a function of \( \Delta IW \) at 2200 K and 5 GPa (see Table 7.3 and section 7.3.2.1). The horizontal line represents the boundary between siderophile and lithophile behavior. See Fig. 7.1 caption for additional details.

Only the EH scenario yields sufficient C in the core to obtain graphite saturation at 5 GPa and 2200 K (Fig. 7.4). However, the estimates for CCGS-metal presented here are upper limits, given the negative pressure dependency of CCGS-metal (Chapter 6) and the central pressure of 36 GPa suggested for Mercury (Hauck II et al., 2013). In addition, assuming Mercury’s core composition to be close to a Fe-Si-C alloy, early crystallization of a solid Fe-rich inner core (e.g. Knibbe and van Westrenen, 2015) would result in significant enrichment of C in the remaining liquid metal, given its extremely low solubility (~0.10 wt.% at 10 GPa and 1550 K) in solid Fe-Si alloys (Deng et al., 2013). Silicon would not strongly fractionate between solid and liquid metal (Deng et al., 2013; Morard et al., 2014), resulting in much lower required bulk C contents to lead to graphite saturation, the exact extent dependent on the size of the solid core. These results show that differentiation of Mercury at highly reduced conditions will result in graphite saturation, if the
core is Si-rich and/or if bulk Mercury was not significantly depleted in C relative to its inferred building blocks. Extensive depletion of volatile elements in Mercury’s building blocks would be at odds with the relatively high abundances of the alkali elements, Cl and S across its surface (Evans et al., 2015; Peplowski et al., 2015a). This model therefore supports the hypothesis of Vander Kaaden and McCubbin (2015) of a graphitic flotation crust in Mercury’s early history.

![Diagram of C abundances in Mercury’s core assuming C-saturated conditions for the three bulk compositions considered at 2200 K and 5 GPa (Table 7.3). Blue lines depict the modeled CCGS$_{metal}$ values calculated using Eq. (6.6) for each considered bulk composition. Horizontal shaded bars or line represent the estimated C contents of Mercury’s core and mantle, calculated using the predictive model of Li et al. (2016). Vertical shaded bars represent the estimated average $\langle f \rangle_0$, value of $\Delta IW = -5.4 \pm 0.4$ of Mercury’s surface (Namur et al., 2016a).](image)

*Fig. 7.3* Calculated C abundances in Mercury’s core assuming C-saturated conditions for the three bulk compositions considered at 2200 K and 5 GPa (Table 7.3). Blue lines depict the modeled CCGS$_{metal}$ values calculated using Eq. (6.6) for each considered bulk composition. Horizontal shaded bars or line represent the estimated C contents of Mercury’s core and mantle, calculated using the predictive model of Li et al. (2016). Vertical shaded bars represent the estimated average $\langle f \rangle_0$, value of $\Delta IW = -5.4 \pm 0.4$ of Mercury’s surface (Namur et al., 2016a).
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Fig. 7.4 Calculated $\text{CCGS}_{\text{metal}}$ values for the three bulk compositions considered as a function of the Si content of Mercury's core at $\Delta W = -5.4 \pm 0.4$, 2200 K and 5 GPa (see Table 7.3 and section 7.3.1). A graphite flotation crust is expected to form above the curved line showing $\text{CCGS}_{\text{metal}}$ for a given Si content.

7.3.2 Constraints on core composition and volatile loss in the AuPB

7.3.2.1 Depletions of VSE in aubrites

Table 7.4 lists the derived average concentrations of the siderophile elements in aubrites based on compiled data of Biswas et al. (1980) and Wolf et al. (1983) for well-characterized aubrites Aubres, Bishopville, Bustee, Cumberland Falls, Khor Temiki, Maya Belwa, Norton County, Peña Blanca Spring and Pesyanoe. Table A.7.1 lists the siderophile element abundances for each of these aubrites. The results are graphically illustrated in Fig. 7.5, where the depletions of VSE and other siderophile elements relative to EH or EL chondrites (Fig. 7.5a) and the required log D values (Fig. 7.5b, Eq. 3.7) are plotted as a function of the 50% condensation temperatures at $10^{-4}$ bar (Lodders, 2003) for an enstatite chondrite bulk composition.

The inferred depletions for most VSE (Zn, Cd, In, Bi, Tl and to a lesser extent Se and Te) are dependent of the assumed bulk composition (Fig. 7.5a). Consideration of an EH chondrite-like bulk composition for the AuPB yields a depletion factor of ~0.01 for these elements, whereas an EL chondritic bulk compositions yields a depletion factor of ~0.1 or higher. In contrast, the depletion factors and required log D values for moderately volatile or refractory elements (Ge, Ga, Sb, Cu, As, Co, Ni) are very similar for both bulk compositions.
Fig. 7.5 (a) The depletions of VSE and other siderophile elements in aubrites, relative to EH or EL chondrites as a function of their 50% condensation $T$ at $10^4$ bar in K (Lodders, 2003) (b) The log $D$ values required to fully explain the depletions of VSE and other siderophile elements in aubrites observed in (a) by core formation as a function of their 50% condensation $T$ at $10^4$ bar in K for an enstatite chondrite bulk composition (Lodders, 2003). The core fractions of the AuPB were considered to be 0.29 and 0.41 by mass in the case of the EL and EH chondritic bulk compositions, respectively, based on the $f^O_2$ value of $\Delta IW = -5.5 \pm 0.3$ inferred for the AuPB interior based on basaltic vitrophyres in aubrites (Fogel, 2005). Errors indicate maximum errors based on 1 SE uncertainties on aubrite abundances (Table 7.4).

7.3.2.2 Constraints on the Si content of the AuPB core

Left panels in Figure 7.6 show the calculated AuPB core- and mantle abundances of Si for both end-member bulk compositions considering either a C-free or a C-saturated core. The overall modeled core Si contents range from 0.4 to 20 wt.% within the $f^O_2$ range of $\Delta IW = -5.5 \pm 0.3$ (Table 7.5). As observed in the Mercury modeling results, the modeled core Si contents are strongly dependent on concentration of C in the core. The addition of C greatly reduces the estimated Si content of the AuPB core. However, the expected AuPB core C concentration is likely very low given the low bulk C contents of enstatite chondrites (<1.3 wt.%; Newsom, 1995). This implies that significant quantities of Si are expected in the AuPB core (6.0 to 20 wt.% for a C-free core; Fig. 7.6 and Table 7.5). Right panels in Fig. 7.6 compare the calculated C content
of the AuPB core and mantle with CCGS\textsubscript{metal} values. All calculated CCGS\textsubscript{metal} values greatly exceed the calculated concentrations of C in the core. This suggests that the formation of a graphitic flotation crust on the AuPB is unlikely. This is the result of a combination of reduced siderophile behavior of Si at the low P-T conditions relevant for asteroidal differentiation, and enhanced CCGS\textsubscript{metal} values at these conditions.

Fig. 7.6 Left panels: calculated Si abundances in the AuPB core and mantle assuming C-free and C-saturated conditions for the EH or EL bulk compositions at 1883 K and 0.1 GPa (Table 7.5). Right panels: Calculated C abundances in the AuPB core assuming C-saturated conditions for the two bulk compositions considered at 1883 K and 0.1 GPa. Blue lines depict the modelled CCGS\textsubscript{metal} values calculated using Eq. (6.6) for each considered bulk composition. Horizontal lines represent the estimated C contents of the AuPB core and mantle, calculated using the predictive model of Li et al. (2016). Vertical shaded bars in all panels represent the \( f_0^2 \) value of \( \DeltaIW = -5.5 \pm 0.3 \) inferred for the AuPB interior based on basaltic vitrophyres in aubrites (Fogel, 2005).

7.3.2.3 Partitioning of volatile elements into the AuPB core?

Using the core compositions as a function of oxygen fugacity derived in the previous sections, the variation of the metal-silicate D values for siderophile elements can be modeled using the 1 GPa interaction coefficients and Eqs. (6.2, 6.5–6.7) reported in Chapter 6. Figures 7.7 and 7.8 show the results, where the exchange coefficient or K\(_0\) calculated for the inferred AuPB redox state of \( \DeltaIW = -5.8 \) to \(-5.2\) are plotted versus the natural logarithm of the corresponding Si content of the AuPB core. It is found that the observed aubrite depletions of the majority of the refractory and moderately volatile elements considered here (Ni, Ge, As, Sb) can be reconciled with AuPB core formation occurring at \( \DeltaIW = -5.8 \) to \(-5.2\) for the corresponding Si contents at this redox state.
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Fig. 7.7 Modeled exchange coefficients or LN K_D values as a function of the natural logarithm of the molar fraction of Si in the AuPB core. Vertical bars represent the ranges of Si in the core from this study for an EH or EL AuPB bulk composition. Horizontal bar represents the full range of required LN K_D values for the various elements while assuming a fO_2 of ΔIW = −5.5±0.3 during AuPB differentiation. Errors represent maximum errors that were calculated using simple error propagation.

However, the depletions of the majority of the most volatile elements considered (Zn, Cd, Ga, In) cannot be reconciled with core formation depletion only (i.e. required LN K_D values are higher than modeled LN K_D values at ∆IW = −5.8 to −5.2 for corresponding Si contents of the AuPB core). Core formation at more reduced conditions than inferred in this study will only increase the offset due to higher Si contents of the core, whereas conditions at more oxidized conditions result in even lower D values of Zn, Cd, Ga, In for a given Si content. This suggests that the observed depletions of these elements are affected by processes other than core formation, such as volatile loss during AuPB differentiation, preferential partitioning in segregated FeS minerals, and/or their (in)compatibility in co-existing silicate minerals.
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**Fig. 7.8** Modeled exchange coefficients or LN $K_0$ values for high valence siderophile elements as a function of the molar fraction of Si in the AuPB core. See Fig. 7.7 caption for additional details.

**Fig. 7.9** Modeled range of $\log D_{Se}^{|melt-sill|}$ as a function of $fO_2$. $D_{Se}^{|melt-sill|}$ were calculated using the parameterizations reported in section 2.3. Vertical shaded bars represent the $fO_2$ value of $\Delta IW = -5.5\pm0.3$ inferred for the AuPB interior based on basaltic vitrophyres in aubrites (Fogel, 2005). Horizontal bars represent the required $\log D_{Se}^{|melt-sill|}$ values while assuming an EH or EL AuPB bulk composition. Errors represent maximum errors that were calculated using simple error propagation.
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Fig. 7.9 shows the predicted log $D_{\text{Se, Te}}^{\text{met-sil}}$ during core formation in the AuPB as a function of $fO_2$. At the inferred $fO_2$ range of AuPB differentiation, both Se and Te behave lithophile. As observed for the other volatile elements, required D values are higher than modeled values, suggesting other depletion mechanisms need to be invoked to explain the observed depletions of Se and Te in aubrites.

7.4 Discussion

7.4.1 The effect of S on core compositional models of reduced bodies

The above models assume the absence of FeS-rich layers in Mercury and the AuPB. A S-rich core and FeS-rich layer in Mercury were previously suggested on the basis of the observed persistence of a partially molten core until the present day and the nature of Mercury's magnetic field (e.g., Hauck et al., 2013). Recent work suggests high S contents in Mercury are not required (e.g., Knibbe and van Westrenen, 2013). The existence of a FeS-rich reservoir would not affect the overall composition of the core of Mercury and/or the AuPB. At highly reducing conditions, S will not significantly partition into Fe-Si-rich alloys, but instead behaves lithophile, like Se and Te (Kilburn and Wood, 1997; Chapter 8). This is also reflected by the high S concentrations on Mercury's surface (Namur et al., 2016a) and the high S concentrations measured in silicate phases in aubrites (Fogel, 1998; 2005). The results presented here for the core compositions of Mercury and the AuPB, as well as the formation of a graphitic flotation crust in Mercury's early history, are therefore largely independent of the occurrence and/or extent of sulfide segregation.

7.4.2 Graphitic flotation crusts: a consequence of reduced differentiation?

Given the low solubility of C in Si-rich Fe-Si alloys as well as in silicate melts at reducing conditions, graphitic flotation crusts may form on reduced rocky bodies. However, it is shown here that graphite saturation is unlikely to occur on smaller differentiated bodies, such as the AuPB and potentially other reduced asteroids. This is mainly due to a decrease in the siderophile behavior of Si with decreasing $P$-$T$, so that less Si will partition into the core and $C_{\text{CGS,metal}}$ values will be higher. It is therefore unlikely that Si contents will be high enough to allow for the required decrease in $C_{\text{CGS,metal}}$ values to produce C-saturated mantles in these small bodies. On the other hand, recent exoplanet observations suggest that some of these planets have core masses similar to Mercury (e.g., K2-229b; Santerne et al., 2018) and that these bodies could be more C-rich than planets in our solar system. The Si partitioning results
and new parameterization of $\text{CCGS}_{\text{metal}}$ (Eq. 6.6) predict that the formation of a graphitic flotation crust on these larger planets is a likely, natural consequence of differentiation under reducing conditions, given that $P$ and $T$ are high enough to allow for sufficient Si partitioning into the cores. In addition, any degree of core solidification will result in an additional enrichment of C in the liquid phase, promoting C-saturation (Deng et al., 2013). It is therefore proposed that formation of graphitic flotation crusts is likely a common process for reduced bodies that are located close to their host star(s) outside our solar system (e.g. Hakim et al., 2018).

### 7.4.3 The nature of VSE depletions in the AuPB

The application of the experimental data from Chapter 6 to models of core formation in the AuPB illustrates the potential of reduced cores as a substantial reservoir for volatile elements. Wolf et al. (1983) also postulated that as much as one third of the bulk AuPB budget of volatile metals Ag, Zn, In, Cd, Bi, Ti may have been sequestered in its Fe-rich core. The remainder was proposed to have been lost through degassing and/or incompatibility of these elements in silicate-dominated magmatic systems. The need for core formation depletion has also been emphasized by Lodders et al. (1993) and Casanova et al. (1993) for other (highly) siderophile elements and from the light Fe isotopic compositions of main-group aubrites (Wang et al., 2014).

Modeling results also show that for all volatile elements considered here (Zn, Cd, Se, Ga, In, Te), their preferential partitioning into a Si-bearing AuPB core is not sufficient to fully explain their depletions in aubrites, so that additional depletion mechanisms are required. One potential mechanism of additional depletion is their preferential partitioning into segregating sulfides. Although there is currently only a limited understanding of how these elements behave geochemically in highly reduced systems with co-existing sulfides, at moderately reducing conditions the VSE all behave chalcophile (Kiseeva and Wood, 2013, 2015; Steenstra et al., 2018b). An important role for sulfides in the behaviour of Zn during AuPB differentiation is suggested by the very high Zn contents of sulfides in aubrites. For example, Lodders et al. (1993) reported concentrations of up to 800 ppm Zn in alabandite (MnS) in the Peña Blanca Spring aubrite. Reported concentrations of Se in FeS minerals in the same aubrites range from 115 to 200 ppm, suggesting (highly) chalcophile behavior of Se in this aubrite. To further quantify the potential effects of sulfide segregation during core formation on volatile element depletions in the AuPB mantle and other reduced achondrites, more experimental data on their sulfide-silicate partitioning behavior at highly reduced conditions are required.
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Another potential mechanism for explaining the VSE depletions in aubrites is volatile loss during or after core formation in the AuPB. Moynier et al. (2011) investigated the Zn isotopic composition of various main group aubrites and reported light Zn isotopic compositions for aubrites, spanning a range of $\delta^{66}\text{Zn} = -5.5$ to $-0.25\%$. This direction of isotopic fractionation is opposite to what would be expected if Zn depletion occurred through formation of a vapor phase, assuming aubrites were derived from a parent body with an EH and/or EL chondrite-like parent body (Moynier et al., 2011). Aubrites also display extreme bulk S isotopic compositions, with $\delta^{34}\text{S}$ values ranging between $-1.35$ to $0.15\%$ (Defouilloy et al., 2016). The latter workers explained the large range and overall light values by segregation of metal and silicates during AuPB differentiation in conjunction with differentiation events as a result of impact events and mixing with impact-related compounds, rather than evaporative fractionation or loss of S through formation of a vapor phase.

Finally, the discrepancies for elements that are more abundant in aubrites than expected given their siderophile and/or chalcophile nature could be due to their compatibility in other crystallizing mineral phases in the AuPB such as enstatite. At present there are no experimentally determined enstatite-melt partitioning data for these elements so this aspect is difficult to quantify. Overall, this work illustrates that Fe-rich cores in reduced bodies are substantial reservoirs for VSE. These reservoirs should not be ignored in interpretations of volatile element depletion signatures in reduced achondrites.

7.5 Conclusions

Using the experimental data set for metal-silicate partitioning under reducing conditions from Chapter 6 expressions were derived to predict the metal-silicate partitioning of Si, Ti, Se and Te as a function of $P-T$ and/or metal/silicate composition. These expressions were used to constrain the core compositions of Mercury and the Aubrite Parent Body (AuPB), while considering different potential bulk planet compositions. The expected core abundances of Si in Mercury's and the AuPB core vary between $\sim4.5$–21 and $\sim0.4$–20 wt.%, respectively, using independent $fO_2$ constraints. The exact abundances of Si in their cores are dependent on $fO_2$, bulk composition and the occurrence of graphite saturation. If the AuPB bulk composition is assumed not to be enriched in C relative to enstatite chondrites, modelling results yield core Si contents of 5.9 to 20 wt.%, depending on the bulk composition considered. Graphite-saturated conditions during AuPB differentiation would result in much lower Si core concentrations (<2.2 wt.% Si). At high Si contents, the CCGS$_{metal}$ for Mercury's core is low. If Mercury's core composition can be approximated with a Fe-Si-C alloy and it crystallized an inner core in its
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Early history, the bulk C contents required for graphite saturation would be even lower. These results confirm the previously proposed geochemical feasibility of a graphitic flotation crust in Mercury’s early history for a variety of bulk Mercury compositions. In case of the AuPB, the formation of a graphitic flotation crust following core/mantle differentiation is unlikely given the less siderophile behavior of Si at the P-T conditions relevant for differentiation in small asteroids. The expected depletions of volatile siderophile elements (VSE) during core formation were calculated using the thermodynamic interaction parameters derived in Chapter 6 previously modelled Si contents and compared with a compilation of VSE analyses for aubrites. These results show that the AuPB core, and by extension other reduced planetary cores, have significant potential of being a significant reservoir for many volatile elements. However, formation of a Fe-Si bearing AuPB core does not explain the depletions of the most volatile elements in aubrites, stressing the need for additional depletion processes such as segregation of sulfide minerals and/or volatile loss during or after AuPB differentiation.

Acknowledgements
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Appendix

A.7.1 Modeling core formation in Mercury and the AuPB

Several measures were taken to obtain a geochemically relevant metal-silicate partition coefficient dataset for Mercury and the AuPB. An important issue is the possibility of different pressure dependencies for different pressure regimes. Previous workers have suggested that the pressure dependency of the metal-silicate partitioning of many elements is distinctly different below <5 GPa relative to the >5 GPa domain (e.g. Sanloup et al., 2011). Comparison of our new data and previously reported data between 1-50 GPa can be used to study the effects of pressure on log $K_{\text{app}}$ Si within a wider pressure range. We find that the pressure dependency of log $K_{\text{app}}$ Si is indeed significantly different at <5 GPa than that for pressures >5 GPa, similar to what has been previously observed for including Ni and Co (Sanloup et al., 2011) (Fig. A.7.1). This is also confirmed by the results of multiple linear regressions on low pressure (<5 GPa) data, high pressure (>5 GPa) data and the combined dataset (Table 7.2 in the main text). It is evident that in the case of Mercury and the AuPB, incorporation of all data would result in erroneous pressure dependencies at the pressures relevant for Mercury. The significantly different pressure dependency is likely due to structural transitions in Fe-rich metals occurring at 5.2 GPa (Sanloup et al., 2011). As the core-mantle boundaries of Mercury and the AuPB are at <5 GPa, we only include experimental data obtained at <5 GPa for Si but also for Ti.

Table 7.2 in the main text lists the new parameterizations for Ti and Si, based on previously reported metal-silicate partitioning data and the data from Chapter 6. Fig. A.7.2 shows a comparison between predicted and calculated metal-silicate partition coefficients Si and Ti.

![Figure A.7.1](image-url)  
*Fig. A.7.1* log $K_{\text{app}}$ Si as a function of pressure. Lines indicate the different pressure trends reported in main text Table 2 for parameterizations using the nbo/t parameter. All data was corrected to a common nbo/t value of 4.
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Fig. A.7.2 Comparison between measured and predicted exchange coefficients for Si and metal-silicate partition coefficients for Ti. Predicted metal-silicate partition coefficients were calculated by using the expressions marked in bold in main text Table 2. Solid line is an identity line plotted for reference. Dotted lines represent 50% deviation from the 1:1 correlation.

Fig. A.7.3 Example of modelled core mass fractions of the AuPB assuming an EH chondritic bulk composition. Core masses become constant at conditions more reducing than ΔIW ~ -3.
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* Classification from Keil (2010)  
Numbers in parentheses are 1SD errors in terms of least digits cited  
Based on Ir abundances (see main text section 7.2.2)  
Based on Te abundances (see main text section 7.2.2)